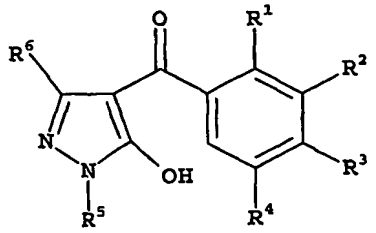
Synergistically acting herbicidal mixtures

The present invention relates to a synergistic herbicidal mixture comprising

A) at least one 3-heterocyclyl-substituted benzoyl derivative of the formula I



I

in which the variables have the following meanings:

R^1, R^3 are halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkylthio, C_1-C_6-alkylsulfinyl or C_1-C_6-alkylsulfonyl;

R^2 is a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-4-yl, isoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl and 4,5-dihydroisoxazol-5-yl; it being possible for the six radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio;

R^4 is hydrogen, halogen or C_1-C_6-alkyl;

R^5 is C_1-C_6-alkyl;

R^6 is hydrogen or C_1-C_6-alkyl;

or one of its environmentally compatible salts;

and

B) two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr;

or one of its environmentally compatible salts;

and, if desired,

C) at least one herbicidal compound from the group of the acetyl-CoA carboxylase inhibitors (ACC), acetolactate synthase inhibitors (ALS), amides, auxin herbicides, auxin transport inhibitors, carotenoid biosynthesis inhibitors, enolpyruvylshikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors, lipid biosynthesis inhibitors, mitosis inhibitors, protoporphyrinogen IX oxidase inhibitors, photosynthesis inhibitors, synergists, growth substances, cell wall biosynthesis inhibitors and a variety of other herbicides;

in a synergistically effective amount.

The invention furthermore relates to herbicidal compositions comprising a herbicidally active amount of a synergistic herbicidal mixture as defined above and at least one liquid and/or solid carrier and, if desired, at least one surfactant.

Moreover, the invention relates to processes for the preparation of these compositions and to a method of controlling undesirable vegetation.

In crop protection products, it is always desirable to increase the specific activity of an active ingredient and the reliability of action. It is an object of the present invention to increase the activity and/or selectivity of the herbicidally active 3-heterocyclyl-substituted benzoyl derivatives of the formula I against undesirable harmful plants.

We have found that this object is achieved by the mixtures defined at the outset. We have furthermore found herbicidal compo-

sitions which comprise these mixtures, processes for their preparation, and methods of controlling undesirable vegetation. In the last-mentioned cases, it is irrelevant whether the herbicidally active compounds of the components A), B) and, if desired, C) are formulated and applied jointly or separately and in which sequence they are applied in the case of separate application.

The mixtures according to the invention show a synergistic effect; the compatibility of the herbicidally active compounds of components A), B) and, if desired, C) for certain crop plants is generally retained.

Suitable components C are, as acetyl-CoA carboxylase inhibitors (ACC), for example, cyclohexenone oxime ethers, phenoxyphenoxypropionic esters or arylaminopropionic acids. The acetolactate synthase inhibitors (ALS) include, inter alia, imidazolinones, pyrimidyl ethers, sulfonamides or sulfonyl ureas. Relevant auxin herbicides are, inter alia, pyridine carboxylic acids, 2,4-D or benazolin. Lipid biosynthesis inhibitors which are used are, inter alia, anilides, chloroacetanilides, thioureas, benfuresate or perfluidone. Suitable mitosis inhibitors are, inter alia, carbamates, dinitroanilines, pyridines, butamifos, chlorthaldimethyl (DCPA) or maleic hydrazide. Examples of protoporphyrinogen IX oxidase inhibitors are, inter alia, diphenyl ethers, oxadiazoles, cyclic imides or pyrazoles. Suitable photosynthesis inhibitors are, inter alia, propanil, pyridate, pyridafol, benzothiadiazinones, dinitrophenols, dipyridylenes, ureas, phenols, chloridazon, triazine, triazinone, uracils or biscarbamates. The synergists are, inter alia, oxiranes. Examples of suitable growth substances are aryloxyalkanoic acids, benzoic acids or quinolinecarboxylic acids. The group "various other herbicide" is to be understood as meaning, inter alia, the classes of the active ingredients dicloropropionic acids, dihydrobenzofurans, phenylacetic acids and individual herbicides mentioned below whose mechanism of action is not (fully) understood.

Other suitable components C) are active compounds selected from the group of the amides, auxin transport inhibitors, carotenoic

biosynthesis inhibitors, enolpyruvylshikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors and cell wall synthesis inhibitors.

Examples of herbicides which can be used in combination with the 3-heterocyclyl-substituted benzoyl derivatives of formula I and the compound of formula II according to the present invention are, inter alia:

C1 acetyl-CoA carboxylase inhibitors (ACC), for example

- cyclohexenone oxime ethers, such as alloxydim, clethodim, cloproxydim, cycloxydim, sethoxydim, tralkoxydim, butroxydim, clefoxydim or tepraloxydim;
- phenoxyphenoxypropionic esters, such as clodinafop-propargyl (and, if appropriate, cloquintocet), cyhalofop-butyl, diclofop-methyl, fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenthiapropethyl, fluazifop-butyl, fluazifop-P-butyl, haloxyfop-ethoxyethyl, haloxyfop-methyl, haloxyfop-P-methyl, isoxapyrifop, propaquizafop, quizalofop-ethyl, quizalofop-P-ethyl or quizalofop-tefuryl; or
- arylaminopropionic acids, such as flamprop-methyl or flamprop-isopropyl;

C2 acetolactate synthase inhibitors (ALS), for example

- imidazolinones, such as imazapyr, imazaquin, imazamethabenz-methyl (imazame), imazamox, imazapic, imazethapyr or imazamethapyr;
- pyrimidyl ethers, such as pyrithiobac-acid, pyrithiobac-sodium, bispyribac-sodium, KIH-6127 or pyribenzoxym;
- sulfonamides, such as florasulam, flumetsulam or metosulam; or
- sulfonylureas, such as amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, flazasulfuron, halosulfuron-methyl, imazosulfuron, metsulfuron-methyl, nicosulfuron, primisulfuron-methyl, prosulfuron, pyrazosulfuron-

ethyl, rimsulfuron, sulfometuron-methyl, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflusulfuron-methyl, N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]amino]carbonyl]-2-(trifluoromethyl)-benzenesulfon-amide, sulfosulfuron or iodosulfuron;

C3 amides, for example
- allidochlor (CDAA), benzoylprop-ethyl, bromobutide, chlorthiamid, diphenamid, etobenzanid (benzchlomet), fluthiamide, fosamin or monalide;

C4 auxin herbicides, for example
- pyridinecarboxylic acids, such as clopyralid or picloram; or
- 2,4-D or benazolin;

C5 auxin transport inhibitors, for example
- naptalame or diflufenzopyr;

C6 carotenoid biosynthesis inhibitors, for example
- benzofenap, clomazone (dimethazone), diflufenican, fluorochloridone, fluridone, pyrazolynate, pyrazoxyfen, isoxaflutole, isoxachlortole, mesotrione, sulcotrione (chlormesulone), ketospiradox, flurtamone, norflurazon or amitrol;

C7 enolpyruvylshikimate-3-phosphate synthase inhibitors (EPSPS), for example
- glyphosate or sulfosate;

C8 glutamine synthetase inhibitors, for example
- bilanafos (bialaphos) or glufosinate-ammonium;

C9 lipid biosynthesis inhibitors, for example
- anilides, such as anilofos or mefenacet;
- chloroacetanilides, such as dimethenamid, S-dimethenamid, acetochlor, alachlor, butachlor, butenachlor, diethatyl-ethyl, dimethachlor, metazachlor, metolachlor,

S-metolachlor, pretilachlor, propachlor, prynachlor, terbuchlor, thenylchlor or xylachlor;

- thioureas, such as butylate, cycloate, di-allate, dimepiperate, EPTC, esprocarb, molinate, pebulate, prosulfocarb, thiobencarb (benthiocarb), tri-allate or vernolate; or
- benfuresate or perfluidone;

C10 mitosis inhibitors, for example

- carbamates, such as asulam, carbetamid, chlorpropham, orbencarb, pronamid (propyzamid), propham or tiocarbazil;
- dinitroanilines, such as benefin, butralin, dinitramin, ethalfluralin, fluchloralin, oryzalin, pendimethalin, prodiamine or trifluralin;
- pyridines, such as dithiopyr or thiazopyr; or
- butamifos, chlorthal-dimethyl (DCPA) or maleic hydrazide;

C11 protoporphyrinogen IX oxidase inhibitors, for example

- diphenyl ethers, such as acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlornitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen or oxyfluorfen;
- oxadiazoles, such as oxadiargyl or oxadiazon;
- cyclic imides, such as azafenidin, butafenacil, carfentrazone-ethyl, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone or thidiazimin; or
- pyrazoles, such as ET-751, JV 485 or nipyraclofen;

C12 photosynthesis inhibitors, for example

- propanil, pyridate or pyridafol;
- benzothiadiazinones, such as bentazone;
- dinitrophenols, for example bromofenoxim, dinoseb, dinoseb-acetate, dinoterb or DNOC;
- dipyridylenes, such as cyperquat-chloride, difenzoquat-methylsulfate, diquat or paraquat-dichloride;

- ureas, such as chlorbromuron, chlorotoluron, difenoxuron, dimefuron, diuron, ethidimuron, fenuron, fluometuron, isoproturon, isouron, linuron, methabenzthiazuron, methazole, metobenzuron, metoxuron, monolinuron, neburon, siduron or tebuthiuron;
- phenols, such as bromoxynil or ioxynil;
- chloridazon;
- triazines, such as ametryn, atrazine, cyanazine, desmetryn, dimethamethryn, hexazinone, prometon, prometryn, propazine, simazine, simetryn, terbumeton, terbutryn, terbutylazine or trietazine;
- triazinones, such as metamitron or metribuzin;
- uracils, such as bromacil, lenacil or terbacil; or
- biscarbamates, such as desmedipham or phenmedipham;

C13 synergists, for example

- oxiranes, such as tridiphane;

C14 growth substances, for example

- aryloxyalkanoic acids, such as 2,4-DB, clomeprop, dichlorprop, dichlorprop-P (2,4-DP-P), fluoroxypyr, MCPA, MCPB, mecoprop, mecoprop-P or triclopyr;
- benzoic acids, such as chloramben or dicamba; or
- quinolinecarboxylic acids, such as quinclorac or quinmerac;

C15 cell wall synthesis inhibitors, for example

- isoxaben or dichlobenil;

C16 various other herbicides, for example

- dichloropropionic acids, such as dalapon;
- dihydrobenzofurans, such as ethofumesate;
- phenylacetic acids, such as chlorfenac (fenac); or
- aziprotryn, barban, bensulide, benzthiazuron, benzofluor, buminafos, buthidazole, buturon, cafenstrole, chlorbufam, chlorfenprop-methyl, chloroxuron, cinmethylin, cumyluron, cycluron, cyprazine, cyprazole, dibenzyluron, dipropetryn, dymron, eglinazin-ethyl, endothall, ethiozin, flucabazone, fluorbentranil, flu-

poxam, isocarbamid, isopropalin, karbutilate, mefluidide, monuron, napropamide, napropanilide, nitralin, oxaciclomefone, phenisopham, piperophos, procyazine, profluralin, pyributicarb, secbumeton, sulfallate (CDEC), terbucarb, triaziflam, triazofenamid or trimeturon;

or their environmentally compatible salts.

The 3-heterocyclyl-substituted benzoyl derivatives of the formula I are disclosed in WO 96/26206, WO 97/41116, WO 97/41117, WO 97/41118 and WO 98/31681.

The herbicidally active compounds from amongst groups B and C1 to C16 are described, for example, in

- "Herbizide [Herbicides]", Hock, Fedtke, Schmidt, 1st edition, Thieme 1995 (s. "quinclorac" p. 238, "molinat" p. 32, "butachlor" p. 32, "pretilachlor" p. 32, "dithiopyr" p. 32, "mefenacet" p. 32, "fenoxapropethyl" p. 216, "dimepiperate" p. 32, "pyrazolynate" p. 146, "pyrazoxyfen" p. 146, "bensulfuronmethyl" p. 31, "pyrazosulfuron-ethyl" p. 31, "cinosulfuron" p. 31, "benfuresate" p. 233, "bromobutide" p. 243, "dymron" p. 243, "dimethyametryn" p. 118, "esprocarb" p. 229, "pyributicarb" p. 32, "cinemthylin" p. 32, "propanil" p. 32, "2,4-D" p. 30, "bentazon" p. 30, "azimsulfuron (DPX-A-8947)" p. 175, "mecoprop-P" p. 237, "chlorpropham" p. 205, "ethoxyfen" p. 30, "haloxyfop-P-methyl" p. 38, "haloxyfop-ethoxyethyl" p. 38, "flumiclorac-pentyl" p. 35, "flupropacil" p. 143, "nipyraclofen" p. 145, "metosulam" p. 33, "ethametsulfuron-methyl" p. 36, "thifensulfuron-methyl" p. 35, "pyrithiobac acid" p. 181);

- "Agricultural Chemicals", Book II Herbicides, 1993 (s. "thiobencarb" p. 85, "benzofenap" p. 221, "napropanilid" p. 49, "piperophos" p. 102, "anilofos" p. 241, "imazosulfuron (TH-913)" p. 150, "etobenzamid (HW-52)" p. 54, "sulcotrione (ICIA-0051)" p. 268, "poast" p. 253, "focus" p. 222, "dimethenamid" p. 48, "sulfosate" p. 236, "2,4-DB" p. 10, "di-

chlorprop-P" p. 6, "flupoxam" p. 44, "prosulfocarb" p. 84, "quinmerac" p. 233, "metazachlor" p. 64, "flurtamone" p. 265, "bromofenoxim" p. 228, "fomesafen" p. 248, "imazamethabenz-methyl" p. 153, "clodinafop-propargyl" p. 214, "fenoxaprop-P-ethyl" p. 208, "fluazifop-P-butyl" p. 207, "quizalofop-P-ethyl" p. 210, "quizalofop-terfuryl" p. 211, "flumioxazin" p. 43, "flumipropyn" p. 267, "sulfentrazone" p. 261, "thiazopyr" p. 226, "pyrithiobac-sodium" p. 266, "flumetsulam" p. 227, "amidosulfuron" p. 151, "halosulfuron-methyl" p. 148, "rimsulfuron" p. 138, "tribenuron-methyl" p. 139, "triflusulfuron-methyl" p. 137, "primisulfuron-methyl" p. 147);

- "Agricultural Chemicals", Book II Herbicides, 13th Edition (s. "carfenstole" p. 284, "sulfosulfuron" p. 145, "ethoxysulfuron" p. 149, "pyribenzoxym" p. 279, "diflufenzopyr" p. 90, "ET-751" p. 278, "carfentrazone-ethyl" p. 267, "fluthiacetmethyl" p. 277, "imazapic" p. 160, "butenachlor" p. 54, "tiocarbazil" p. 84, "fluthiamide" p. 62, "isoxaflutole" p. 283, "butroxydim" p. 259,)

- "Short Review of Herbicides & PGRs 1991, Hodogaya Chemicals (s. "furyloxyfen" p. 142, "triazofenamid" p. 268, "thenylchlorid (NSK-850)" p. 52, "cumyluron (JC-940)" p. 90, "pendimethalin (AC-92553)" p. 58, "buthidazole" p. 88, "cyprazole" p. 38, "allidochlor" p. 48, "benzoylprop-ethyl" p. 38, "chlorthiamid" p. 150, "diphenamid" p. 34, "flampropmethyl" p. 40, "fosamin" p. 232, "isoxaben" p. 42, "monalide" p. 32, "naptalam" p. 36, "pronamid" p. 34, "bialaphos" p. 234, "glufosinate-ammonium" p. 234, "glyphosate" p. 232, "amitrol" p. 254, "clomeprop p. 20, "dichlorprop" p. 6, "fenoprop" p. 8, "fluroxypyr" p. 156, "MCPA" p. 4, "MCPB" p. 8, "mecoprop" p. 6, "napropamide" p. 16, "triclopyr" p. 154, "chloramben" p. 28, "dicamba" p. 26, "clomazone" p. 268, "diflufenican" p. 42, "fluorochloridone" p. 266, "fluridone" p. 156, "asulam" p. 12, "barban" p. 100, "butylate" p. 106, "carbetamide" p. 6, "chlorobufam" p. 100, "cycloate" p. 108, "desmedipham" p. 104, "di-allate" p. 106, "EPTC" p. 108, "orbencarb" p. 112, "pebulate" p. 106,

"phenisopham" p. 118, "phenmedipham" p. 104, "propham" p. 100, "sulfallate" p. 110, "terbucarb" p. 102, "tri-allate" p. 108, "vernolate" p. 108, "acetochlor" p. 48, "alachlor" p. 46, "diethathyl-ethyl" p.48, "dimethachlor" p. 50, "metolachlor" p. 46, "propachlor" p. 44, "pyrnachlor" p. 44, "terbuchlor" p. 48, "xylachlor" p. 52, "alloxydim" p. 260, "clethodim" p. 270, "cloproxydim" p. 268, "tralkoxydim" p. 270, "dalapon" p. 212, "ethofumesate" p. 124, "benefin" p. 54, "butralin" p. 58, "dinitramin" p. 56, "ethalfluralin" p. 60, "fluchloralin" p. 54, "isopropalin" p. 58, "nitralin" p. 58, "oryzalin" p. 60, "prodiamine" p. 62, "profluralin" p. 54, "trifluralin" p. 54, "dinoseb" p. 128, "dinoseb-acetate" p. 128, "dinoterb" p. 128, "DNOC" p. 126, "acifluorfen-sodium" p. 142, "aclonifen" p. 146, "bifenox" p. 140, "chlornitrofen" p. 138, "difenoxuron" p. 76, "fluorodifen" p. 138, "fluoroglycofen-ethyl" p. 146, "lactofen" p. 144, "nitrofen" p. 136, "nitrofluorfen" p. 140, "oxyfluorfen" p. 140, "cyperquat-chloride" p. 158, "difenzoquat-methylsulfate" p. 160, "diquat" p. 158, "paraquat-dichloride" p. 158, "benzthiazuron" p. 82, "buturon" p. 66, "chlorbromuron" p. 72, "chloroxuron" p. 76, "chlorotoluron" p. 74, "cycluron" p. 84, "dimefuron" p. 88, "diuron" p. 70, "ethidimuron" p. 86, "fenuron" p. 64, "fluometuron" p. 68, "isoproturon" p. 80, "isouron" p. 88, "karbutilate" p. 76, "linuron" p. 72, "methabenzthiazuron" p. 82, "metoxuron" p. 72, "monolinuron" p. 66, "monuron" p. 64, "neburon" p. 72, "siduron" p. 68, "tebuthiuron" p. 86, "trimeturon" p. 64, "isocarbamid" p. 168, "imazamethapyr" p. 172, "imazapyr" p. 170, "imazaquin" p. 170, "imazethapyr" p. 172, "methazole" p. 162, "oxadiazon" p. 162, "tridiphane" p. 266, "bromoxynil" p. 148, "ioxynil" p. 148, "diclofop-methyl" p. 16, "fenthiaprop-ethyl" p. 20, "fluazifop-butyl" p. 18, "haloxyfop-methyl" p. 18, "isoxapyrifop" p. 22, "propaquizafop" p. 24, "quizalofop-ethyl" p. 20, "chlorfenac" p. 258, "chlorfenprop-methyl" p. 258, "chloridazon" p. 174, "maleic hydrazide" p. 162, "norflurazon" p. 174, "pyridate" p. 176, "clopyralid" p. 154, "picloram" p. 154, "chlorimuron-ethyl" p. 92, "chlorsulfuron" p. 92, "flazasulfuron" p. 96, "metsulfuron-methyl" S.92, "nicosulfuron" p. 96, "sulfometu-

ron-methyl" p. 92, "triasulfuron" p. 94, "ametryn" p. 198, "atrazine" p. 188, "aziprotryne" p. 206, "cyanazine" p. 192, "cyprazine" p. 192, "desmetryne" p. 200, "dipropetryn" p. 202, "eglinazine-ethyl" p. 208, "hexazinone" p. 208, "procyazine" p. 192, "prometone" p. 196, "prometryn" p. 196, "propazine" p. 188, "secbumeton" p. 196, "simazine" p. 188, "simetryn" p. 196, "terbumeton" p. 204, "terbutryn" p. 198, "terbutylazine" p. 190, "trietazine" p. 188, "ethiozine" p. 210, "metamitron" p. 206, "metribuzin" p. 202, "bromacil" p. 180, "lenacil" p. 180, "terbacil" p. 180, "benazolin" p. 262, "bensulide" p. 228, "benzofluor" p. 266, "butamifos" p. 228, "DCPA" p. 28, "dichlobenil" p. 148, "endothal" p. 264, "mefluidide" p. 306, "perfluidone" p. 260, "terbuchlor" p. 48);

- "Global Herbicide Directory" First Edition, 1994 (s. "oxadiargyl" p. 96);

- "European Directory of Agrochemical Products" Volume 2 - Herbicides" Fourth Edition (s. "buminafos" p. 255).

- "The Pesticide Maunal, 12th edition, 2000 (s. "bispyribac-sodium" p. 97, "florasulam" p. 420, "cyclosulfamuron" p. 217, "pretilachlor" p. 755)

Moreover, the compound "DEH-112" is disclosed in European Patent Application EP-A 302 203. The compound "tepraloxydim" is described in DE-A 33 36 140; the compound "cinidon-ethyl" in DE-A 36 03 789 and the compound "fluorbentranil" in EP-A 84 893. Other compounds are known from "Brighton Crop Protection Conference - Weeds - 1993" (S. "thidiazimin" p. 29, "AC-322140" p. 41, "KIH-6127" p. 47, "prosulfuron" p. 53, "KIH-2023" p. 61, "metobenzuron" p. 67). The compound "carfenstrole (CH-900)" is mentioned in EP-A 332 133, and the compound N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]amino]-carbonyl]-2-(trifluoromethyl-benzenesulfonamide) is described in PCT/EP 96/03996.

The assignment of the active ingredients to the respective mechanisms of action is based on current knowledge. If several

mechanisms of action apply to one active ingredient, this substance was only assigned to one mode of action.

The 3-heterocyclyl-substituted benzoyl derivatives of the formula I can exist, or be used, in the form of the pure enantiomers and also as racemates or diastereomer mixtures.

The 3-heterocyclyl-substituted benzoyl derivatives of the formula I and/or the herbicidally active compounds from amoungs group B and/or the herbicidally active compounds from amoungs groups C1 to C16 may also exist in the form of their environmentally compatible salts. Suitable salts are, in general, the salts of those cations, or the acid addition salts of those acids, whose cations, or anions, respectively, do not adversely affect the herbicidal action of the active ingredients.

Suitable cations are, in particular, ions of the alkali metals, preferably lithium, sodium and potassium, of the alkaline earth metals, preferably calcium and magnesium, and of the transition metals, preferably manganese, copper, zinc and iron, and also ammonium, it being possible in this case, if desired, for one to four hydrogen atoms to be replaced by C_1-C_4-alkyl, hydroxy-C_1-C_4-alkyl, C_1-C_4-alkoxy-C_1-C_4-alkyl, hydroxy-C_1-C_4-alkoxy-C_1-C_4-alkyl, phenyl or benzyl, preferably ammonium, isopropylammonium, dimethylammonium, diisopropylammonium, tetramethylammonium, tetrabutylammonium, 2-(2-hydroxyeth-1-oxy)eth-1-yl ammonium, di(2-hydroxyeth-1-yl)ammonium, trimethylbenzylammonium, furthermore phosphonium ions, sulfonium ions, preferably tri(C_1-C_4-alkyl)-sulfonium and sulfoxonium ions, preferably, tri(C_1-C_4-alkyl)-sulfoxonium.

Anions of suitable acid addition salts are mainly chloride, bromide, fluoride, hydrogen sulfate, sulfate, dihydrogen phosphate, hydrogen phosphate, nitrate, hydrogen carbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate and the anions of C_1-C_4-alkanoic acids, preferably formate, acetate, propionate and butyrate.

Preferred with regard to the synergistic herbicidal action of the mixtures according to the invention are those 3-heterocyclyl-substituted benzoyl derivatives of the formula I in which the variables have the following meanings, either alone or in combination:

R^1 halogen such as chlorine or bromine, C_1-C_6-alkyl such as methyl or ethyl or C_1-C_6-alkylsulfonyl such as methylsulfonyl or ethylsulfonyl;
especially preferably chlorine, methyl or methylsulfonyl;

R^2 a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-5-yl and 4,5-dihydroisoxazol-3-yl, it being possible for the three radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio;
especially preferably isoxazol-5-yl, 3-methyl-isoxazol-5-yl, 4,5-dihydroisoxazol-3-yl, 5-methyl-4,5-dihydroisoxazol-yl, 5-ethyl-4,5-dihydroisoxazol-3-yl or 4,5-dimethyl-4,5-dihydroisoxazol-3-yl;

R^3 halogen such as chlorine or bromine or C_1-C_6-alkylsulfonyl such as methylsulfonyl or ethylsulfonyl;
especially preferably chlorine, methylsulfonyl or ethylsulfonyl;

R^4 hydrogen or methyl;
especially preferably hydrogen;

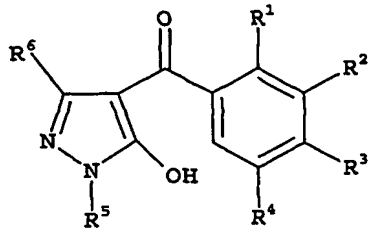
R^5 is C_1-C_6-alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl or 2-methylpropyl;
especially preferably methyl, ethyl or 1-methylethyl;

R^6 hydrogen or C_1-C_6-alkyl, such as methyl or ethyl;
especially preferably hydrogen or methyl.

Very particularly preferred are those 3-heterocyclyl-substituted benzoyl derivatives of the formula Ia, in particular the com-

pounds Ia.1 to Ia.47, which are mentioned in Table 1 which follows:

Table 1

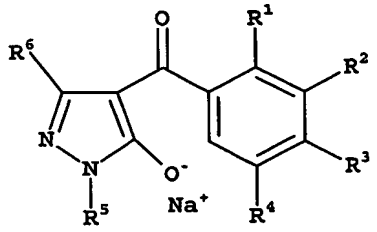


I

No.	R^1	R^2	R^3	R^4	R^5	R^6
Ia.1	Cl	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	CH_3	CH_3
Ia.2	Cl	4,5-dihydroisoxazol-3-yl	Cl	H	CH_3	CH_3
Ia.3	Cl	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.4	Cl	4,5-dihydro-5-methylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.5	Cl	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.6	Cl	4,5-dihydro-5-ethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.7	Cl	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.8	Cl	4,5-dihydro-5-chloromethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.9	Cl	4,5-dihydro-5-ethoxyisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.10	Cl	4,5-dihydro-5-methoxyisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.11	Cl	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.12	Cl	4,5-dihydro-5-thioethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.13	Cl	4,5-dihydro-5-trifluoromethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.14	Cl	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.15	Cl	4,5-dihydroisoxazol-3-yl	Cl	H	C_2H_5	H
Ia.16	Cl	4,5-dihydro-5-methylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.17	Cl	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.18	Cl	4,5-dihydro-5-ethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.19	Cl	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.20	Cl	4,5-dihydro-5-chloromethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.21	Cl	4,5-dihydroisoxazol-3-yl	$SOCH_3$	H	C_2H_5	H
Ia.22	Cl	4,5-dihydro-5-ethoxyisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.23	Cl	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.24	Cl	4,5-dihydro-5-thioethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.25	Cl	4,5-dihydro-5-trifluoromethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H

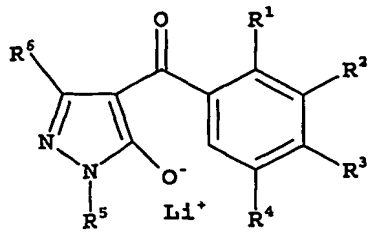
Ia.26	Cl	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	i-C_4H_9	H
Ia.27	CH_3	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	CH_3	CH_3
Ia.28	CH_3	4,5-dihydroisoxazol-3-yl	Cl	H	CH_3	CH_3
Ia.29	CH_3	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.30	CH_3	4,5-dihydro-5-methylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.31	CH_3	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.32	CH_3	4,5-dihydro-5-ethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.33	CH_3	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.34	CH_3	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.35	CH_3	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO_2CH_3	H	CH_3	H
Ia.36	CH_3	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.37	CH_3	4,5-dihydroisoxazol-3-yl	Cl	H	C_2H_5	H
Ia.38	CH_3	4,5-dihydro-5-methylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.39	CH_3	4,5-dihydro-5,5-dimethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.40	CH_3	4,5-dihydro-5-ethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.41	CH_3	4,5-dihydro-5,5-diethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.42	CH_3	4,5-dihydro-4,5-dimethylisoxazol-3-yl	SO_2CH_3	H	C_2H_5	H
Ia.43	CH_3	4,5-dihydroisoxazol-3-yl	SO_2CH_3	H	i-C_4H_9	H
Ia.44	Cl	3-methylisoxazol-5-yl	SO_2CH_3	H	CH_3	H
Ia.45	Cl	3-methylisoxazol-5-yl	SO_2CH_3	H	C_2H_5	H
Ia.46	CH_3	3-methylisoxazol-5-yl	SO_2CH_3	H	CH_3	H
Ia.47	CH_3	3-methylisoxazol-5-yl	SO_2CH_3	H	C_2H_5	H

- Also very particularly preferred are the compounds Ib, in particular the compounds Ib.1 to Ib.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the sodium salt:



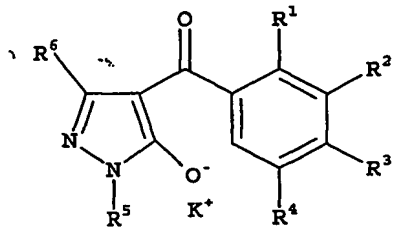
Ib

- Also very particularly preferred are the compounds Ic, in particular the compounds Ic.1 to Ic.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the lithium salt:



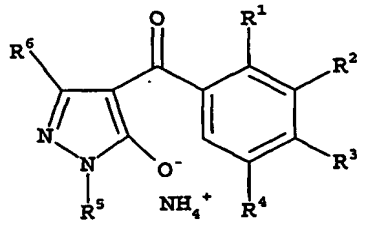
Ic

- Also very particularly preferred are the compounds Id, in particular the compounds Id.1 to Id.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the potassium salt:



Id

- Also very particularly preferred are the compounds Ie, in particular the compounds Ie.1 to Ie.47, which differ from the compounds Ia.1 to Ia.47 only by the fact that they are present as the ammonium salt:



Ie

- Very particularly preferred are, especially, the compounds Ia, especially the compounds Ia.1 to Ia.47.

- Very particularly preferred are, moreover, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I, where

R^4 is hydrogen.

- Very particularly preferred are, moreover, the 3-heterocyclyl substituted benzoyl derivatives of the formula I where

R^2 is a heterocyclic radical selected from the group: isoxazol-3-yl, isoxazol-4-yl and isoxazol-5-yl, it being possible for the three radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio.

Very particularly preferred are, especially, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I, where

R^2 is isoxazol-3-yl which can be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio;

R^4 is hydrogen.

Very particularly preferred are also, especially, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

R^2 is isoxazol-5-yl, which can be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio;

R^4 is hydrogen.

Most particularly preferred is 4-[2-chloro-3-(3-methyl-isoxazol-5-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

Most particularly preferred is also 4-[2-methyl-3-(3-methyl-isoxazol-5-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

- Very particularly preferred are, moreover, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

R^2 is a heterocyclic radical selected from the group: 4,5-dihydroisoxazol-3-yl, 4,5-dihydroisoxazol-4-yl and 4,5-dihydroisoxazol-5-yl, it being possible for the three radicals mentioned to be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio.

Very particularly preferred are, especially, the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

R^2 is 4,5-dihydroisoxazol-3-yl which can be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio;

R^4 is hydrogen.

Most particularly preferred are the 3-heterocyclyl-substituted benzoyl derivatives of the formula I where

R^1 is halogen or C_1-C_6-alkyl; and

R^2 is 4,5-dihydroisoxazol-3-yl which can be unsubstituted or mono- or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-haloalkyl, C_1-C_4-haloalkoxy or C_1-C_4-alkylthio;

R^3 is C_1-C_6-alkylsulfonyl;

R^4 is hydrogen.

Most especially preferred is 4-[2-chloro-3-(4,5-dihydro-isoxazol-3-yl)-4-methylsulfonylbenzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

Most particularly preferred is also 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole.

Preferred with regard to the synergistic herbicidal action of the mixtures according to the invention are those mixtures comprising as component B) imazapyr and imazethapyr, or imapzapyr and imazapic; especially preferred are those mixtures comprising as component B) imazapyr and imazethapyr.

In a further preferred embodiment, the synergistic herbicidal mixture comprises, three herbicidal active compounds, a compound of formula I (component A) and two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazetapyr (component B).

- For particular preferred embodiments, the respective preferences described above apply analogously.

In particular the synergistic herbicidal mixture comprises as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole and two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr (component B).

Especially the synergistic herbicidal mixture comprises as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole and as component B) imazapyr and imazethapyr.

In a further embodiment the synergistic herbicidal mixture especially comprises as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-

hydroxy-1H-pyrazole and as component B) imazapyr and imazapic.

In a further preferred embodiment, the synergistic herbicidal mixture comprises, at least four herbicidal active compounds, a compound of formula I (component A), two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazethapyr (component B), and

C) at least one herbicidal compound from the group of the acetyl-CoA carboxylase inhibitors (ACC), acetolactate synthase inhibitors (ALS), amides, auxin herbicides, auxin transport inhibitors, carotenoid biosynthesis inhibitors, enolpyruvyl-shikimate 3-phosphate synthase inhibitors (EPSPS), glutamine synthetase inhibitors, lipid biosynthesis inhibitors, mitosis inhibitors, protoporphyrinogen IX oxidase inhibitors, photosynthesis inhibitors, synergists, growth substances, cell wall biosynthesis inhibitors and a variety of other herbicides.

With a view to the synergistic herbicidal action of the mixtures comprising a component A), B) and C) according to the invention, compounds from amongst groups C1 to C14 or C16, preferably from amongst groups C9 and C12, are preferred as component C).

In particular, compounds from amongst the classes of active ingredients mentioned below are preferred, or the following compounds are very particularly preferred:

C1 acetyl-CoA carboxylase inhibitors (ACC):

- cyclohexenone oxime ethers, in particular cycloxydim, sethoxydim or tralkoxydim, preferably sethoxydim or tralkoxydim; or
- phenoxyphenoxypropionic esters, in particular clodinafop-propargyl (and, if appropriate, cloquintocet), fenoxaprop-ethyl or fenoxaprop-P-ethyl, preferably clodinafop-propargyl (and, if appropriate, cloquintocet) or fenoxaprop-P-ethyl;

C2 acetolactate synthase inhibitors (ALS):
- imidazolinones, in particular imazapyr, imazaquin, imazamethabenz, imazethapyr or imazamox, preferably imazapyr;
- pyrimidyl ethers, in particular pyrithiobac sodium;
- sulfonamides, in particular florasulam, flumetsulam or metosulam, preferably metosulam; or
- sulfonylureas, in particular halosulfuron-methyl, nicosulfuron, primisulfuron-methyl, prosulfuron, rimsulfuron, thifensulfuron-methyl, tribenuron-methyl, N-[[[4-methoxy-6-(trifluoromethyl)-1,3,5-triazin-2-yl]-amino]carbonyl]-2-(trifluoromethyl)-benzenesulfonamide or sulfosulfuron;

C3 amides:
- fluthiamide;

C4 auxin herbicides:
- pyridinecarboxylic acids, in particular clopyralid; or
- 2,4-D;

C5 auxin transport inhibitors:
- diflufenzopyr;

C6 carotenoid biosynthesis inhibitors:
- isoxaflutole, mesotrione, isoxachloride, ketospiradox or sulcotrione (chlormesulone), in particular isoxaflutole or sulcotrione;

C7 enolpyruvylshikimate-3-phosphate synthase inhibitors (EPSPS):
- glyphosate or sulfosate;

C8 glutamin synthetase inhibitors:
- glufosinate-ammonium;

C9 lipid biosynthesis inhibitors:

- chloroacetanilides, in particular dimethenamid, S-dimethenamid, acetochlor, metolachlor or S-metolachlor,
- thioureas, in particular benthiocarb;

C10 mitosis inhibitors:
- dinitroanilines, in particular pendimethalin;

C11 protoporphyrinogen IX oxidase inhibitors:
- diphenyl ethers, in particular acifluorfen or acifluorfen-sodium;
- oxadiazoles, in particular oxadiargyl; or
- cyclic imides, in particular butafenacil, carfentrazone-ethyl, cinidon-ethyl or flumiclorac-pentyl, preferably carfentrazone-ethyl, cinidon-ethyl or flumidorac-pentyl;
- pyrazoles, in particular JV 85;

C12 photosynthesis inhibitors:
- pyridate or pyridafol, in particular pyridate;
- benzothiadiazinones, in particular bentazone;
- dipyridylenes, in particular paraquat-dichloride;
- ureas, in particular diuron or isoproturon, preferably diuron;
- phenols, in particular bromoxynil;
- chloridazone;
- triazines, in particular atrazine or terbutylazine; or
- triazinones, in particular metribuzin;

C13 synergists:
- oxiranes, in particular tridiphane;

C14 growth substances:
- aryloxyalkanoic acids, in particular fluoroxypyr, MCPA or mecoprop-P;
- benzoic acids, in particular dicamba; or
- quinolinecarboxylic acids, in particular quinclorac;

C16 various other herbicides:

- triaziflam.

In particular, compounds from amongst the classes of active ingredients mentioned below are preferred, or the following compounds are very particularly preferred.

C9 lipid biosynthesis inhibitors:

- chloroacetanilides, in particular dimethenamid, S-dimethenamid, acetochlor, metolachlor or S-metolachlor;

C12 photosynthesis inhibitors:

- pyridate;
- benzothiadiazinones, in particular bentazone;
- dipyridylenes, in particular paraquat-dichloride;
- ureas, in particular diuron or isoproturon, preferably diuron;
- phenols, in particular bromoxynil;
- chloridazon;
- triazines, in particular atrazine or terbutylazine; or
- triazinones, in particular metribuzin;

For particular preferred embodiments, the respective preferences described above apply analogously.

Especially preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazetapyr, in particular imazapyr and imazetapyr or imazetapyr and imazapic; and as component C a herbicidal compound from the group C9, in particular a chloroacetanilide, especially acetochlor.

In particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazetapyr; and as component C a chloroacetanilide, especially acetochlor.

In particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazapic; and as component C a chloroacetanilide, especially acetochlor.

Also especially preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B two herbicides selected from the group including imazapyr, imazaquin, imazamethabenz-methyl, imazamox, imazapic and imazetapyr, in particular imazapyr and imazetapyr or imazapyr and imazapic; and as component C a herbicidal compound from the group C12, in particular a triazine, especially atrazine, or a benzothiadiazinone, especially bentazone.

In particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazetapyr; and as component C a triazine, especially atrazine.

Also in particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazetapyr; and as component C a benzothiadiazinone, especially bentazone.

Also in particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazapic; and as component C a triazine, especially atrazine.

Also in particular preferred are synergistic herbicidal mixtures which comprise as component A 4-[2-methyl-3-(4,5-dihydroisoxazol-3-yl)-4-methylsulfonyl-benzoyl]-1-methyl-5-hydroxy-1H-pyrazole; as component B imazapyr and imazapic; and as component C a benzothiadiazinone, especially bentazone.

The present invention also extends to herbicidal compositions which comprise a herbicidally active amount of a synergistic herbicidal mixture (comprising components A), B) and, if desired, C) as described above), at least one liquid and/or solid carrier and, if desired, at least one surfactant.

The herbicidal compositions and synergistic herbicidal mixtures according to the invention can effect very good control of broad-leaved weeds and grass weeds in crops such as maize, cereals, rice and soya without damaging the crop plants, an effect observed especially even at low rates of application.

Taking into consideration the variety of application method in question, the herbicidal compositions and synergistic herbicidal mixtures according to the invention can additionally be employed in a further number of crop plants for eliminating undesirable plants. Examples of suitable crops are the following:
Allium cepa, Ananas comosus, Arachis hypogaea, Asparagus officinalis, Beta vulgaris ssp. altissima, Beta vulgaris ssp. rapa, Brassica napus var. napus, Brassica napus var. napobrassica, Brassica rapa var. silvestris, Camellia sinensis, Carthamus tinctorius, Carya illinoinensis, Citrus limon, Citrus sinensis, Coffea arabica (Coffea canephora, Coffea liberica), Cucumis sativus, Cynodon dactylon, Daucus carota, Elaeis guineensis, Fragaria vesca, Glycine max, Gossypium hirsutum, (Gossypium arboreum, Gossypium herbaceum, Gossypium vitifolium), Helianthus annuus, Hevea brasiliensis, Hordeum vulgare, Humulus lupulus, Ipomoea batatas, Juglans regia, Lens culinaris, Linum usitatissimum, Lycopersicon lycopersicum, Malus spp., Manihot esculenta, Medicago sativa, Musa spp., Nicotiana tabacum (N.rustica), Olea europaea, Oryza sativa, Phaseolus lunatus, Phaseolus vulgaris, Picea abies, Pinus spp., Pisum sativum, Prunus avium, Prunus

persica, Pyrus communis, Ribes sylvestre, Ricinus communis, Saccharum officinarum, Secale cereale, Solanum tuberosum, Sorghum bicolor (s. vulgare), Theobroma cacao, Trifolium pratense, Triticum aestivum, Triticum durum, Vicia faba, Vitis vinifera und Zea mays.

Moreover, the herbicidal compositions and synergistic herbicidal mixtures according to the invention can also be used in crops which tolerate the action of herbicides due to breeding, including genetic engineering methods.

The mixtures according to the invention, or the herbicidal compositions comprising them, can be employed, for example, in the form of directly sprayable aqueous solutions, powders, suspensions, also highly-concentrated aqueous, oily or other suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading or granules, by means of spraying, atomizing, dusting, spreading or pouring.

The use forms depend on the intended purposes; in any case, they should guarantee the finest possible distribution of the active ingredients according to the invention.

Suitable inert auxiliaries are mineral oil fractions of medium to high boiling point such as kerosene and diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. paraffins, tetrahydronaphthalene, alkylated naphthalenes and their derivatives, alkylated benzenes and their derivatives, alcohols such as methanol, ethanol, propanol, butanol and cyclohexanol, ketones such as cyclohexanone, strongly polar solvents, such as N-methylpyrrolidone and water.

Aqueous use forms can be prepared from emulsion concentrates, suspensions, pastes, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of wetting agent, tackifier, dispersant or emulsifier. However, it is also possi-

ble to prepare concentrates composed of active substance, wetting agent, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and these concentrates are suitable for dilution with water.

Suitable surfactants are the alkali metal, alkaline earth metal and ammonium salts of aromatic sulfonic acids, e.g. ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, of alkyl- and alkylaryl sulfonates, of alkyl sulfates, lauryl ether sulfates and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and of fatty alcohol glycol ether, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene, or of the naphthalenesulfonic acids, with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl and tributylphenyl polyglycol ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignin-sulfite waste liquors or methylcellulose.

Powders, materials for spreading and dusts can be prepared by mixing or concomitantly grinding the synergistic herbicidal mixture or the individual active ingredients with a solid carrier.

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Solid carriers are mineral earths such as silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic material, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas and products of vegetable origin such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The concentrations of the mixtures according to the invention in the ready-to-use products can be varied within wide ranges. In

general, the formulations comprise from 0.01 to 95% by weight, preferably 0.5 to 90% by weight, of the mixture according to the invention.

The components A) and B) and, if desired, C) can be formulated jointly, but also separately, and/or applied to the plants, their environment and/or seeds jointly or separately. It is preferable to apply the active ingredients simultaneously. However, it is also possible to apply them separately.

Also the two herbicides of component B) can be formulated separately, and/or applied to the plants, their environment and/or seeds jointly or separately.

Moreover, it may be advantageous to apply the herbicidal compositions and synergistic herbicidal mixtures according to the invention, jointly or separately, with additional other crop protection agents, for example with pesticides or agents for controlling phytopathogenic fungi or bacteria. Also of interest is the miscibility with mineral salt solutions which are employed for treating nutritional and trace element deficiencies. Non-phytotoxic oils and oil concentrates can also be added.

The mixtures according to the invention and the herbicidal compositions can be applied pre- or post-emergence. If the active ingredients are less well tolerated by certain crop plants, application techniques may be used in which the herbicidal compositions are sprayed, with the aid of the spray apparatus, in such a way that they come into as little contact, if any, with the leaves of the sensitive crop plants while reaching the leaves of undesirable plants which grow underneath, or the bare soil (post-directed, lay-by).

In the case of a post-emergence treatment of the plants, the herbicidal compositions according to the invention are preferably applied by foliar application. Application may be effected, for example, by usual spraying techniques with water as the carrier, using amounts of spray mixture of approx. 100 to 1000 l/ha. The compositions may also be applied by the so-called

"low-volume" and "ultra-low-volume" methods, or in the form of so-called granules.

As a rule, the synergistic herbicidal mixtures comprise components A), B) and, if desired, C) in such weight ratios that the synergistic effect takes place.
The ratios of component A) and B) in the mixture preferably range from 1:0.001 to 1:500, preferably from 1:0.01 to 1:100, particularly preferably from 1:0.1 to 1:50.
The ratios of components A) and C) in the mixture preferably range from 1:0.002 to 1:800, preferably from 1:0.003 to 1:250, especially from 1:0.003 to 1:160, particularly preferably from 1:0.02 to 1:250, especially particularly preferably from 1:0.02 to 1:160.

The rate of application of pure synergistic herbicidal mixture, i.e. without formulation auxiliaries, amounts to 0.2 to 5000 g/ha, especially to 1 to 2000 g/ha, preferably to 2 to 2000 g/ha, in particular to 8 to 1500 g/ha, of active substance (a.s.), depending on the intended aim, the season, the target plants and growth stage.

The rate of application of 3-heterocyclyl-substituted benzoyl derivative of the formula I is 0.1 to 250 g/ha, as a rule 0.5 to 250 g/ha, especially 5 to 250 g/ha, preferably 10 to 150 g/ha, of active substance (a.s.).

The preferred rate of application of component B) is 0.1 to 250 g/ha, as a rule 0.5 to 120 g/ha, especially 1 to 120 g/ha, preferably 10 to 100 g/ha, of active substance (a.s.)

The preferred application rate of the active ingredients of the optional component C) are compiled in Table 2.

Table 2

Component C	Class of active ingredient	Active ingredient	Rate of application (g/ha)
C1 acetyl-CoA carboxylase inhibitors			25-400
	cyclohexenone oxime ethers		100-400
		cycloxydim	100-400
		sethoxydim	100-400
		tralkoxydim	100-400
	phenoxyphenoxypropionic esters		25-300
		clodinafpop-P-propargyl[a]	25-100
		fenoxaprop–ethyl	50-300
		fenoxaprop-P-ethyl	25-150
C2 acetolactate synthase inhibitors (ALS)			0.2–800
	imidazolinones		0.2–800
		imazapyr	0.3-400
		imazaquin	0.5-300
		imazamethabenz	1-800
		imazapic	0.2-400
		imazethapyr	0.3–150
		imazamox	0.2–120
	pyrimidyl ethers		2-120
		pyrithiobac-sodium	2-120
	sulfonamides		1-225
		florasulam	1–20

		flumetsulam	25-225
		metosulam	1–60
	sulfonylureas		1-120
		halosulfuron-methyl	5-120
		nicosulfuron	1-120
		primisulfuron-methyl	10-120
		prosulfuron	10-120
		rimsulfuron	5-120
		thifensulfuron-methyl	10-60
		tribenuron-methyl	10-60
		N-[[[4-methoxy-6-(trifluoro-methyl)-1,3,5-triazin-2-yl]amino]-carbonyl]-2-(trifluoromethyl)-benzenesulfonamide	5-120
		sulfosulfuron	10-60
C3 amides			250-2000
	-	fluthiamide	250-2000
C4 auxin herbicides			25-750
	pyridinecarboxylic acids		25-750
		clopyralid	25-750
	-	2,4-D	50-750
C5 auxin transport inhibitors			15-100
	-	diflufenzopyr	15-100
C6 carotenoid biosynthesis inhibitors			25-600
	-	isoxaflutole	25-200

	-	sulcotrione	100-600
	-	mesotrione	25-300
	-	isoxachlortole	25-200
	-	ketospiradox	25-300
C7 enolpyruvylshikimat-3-phosphate synthase inhibitors (EPSPS)			360-1080
	-	glyphosate	360-1080
	-	sulfosate	360-1080
C8 glutamine synthetase inhibitors			10-600
	-	glufosinate-ammonium	10-600
C9 lipid biosynthesis inhibitors			60-4000
	chloroacetanilides		60-4000
		dimethenamid	60-2000
		S-dimethenamid	60-2000
		acetochlor	250-4000
		metolachlor	60-4000
		S-metolachlor	60-4000
	thioureas		100-4000
		benthiocarb	1000-4000
C10 mitosis inhibitors			375-3000
	dinitroanilines		375-3000
		pendimethalin	375-3000
C11 protoporphyrinogen IX oxidase inhibitors			0.5-600
	diphenyl ethers		50-300

		acifluorfen	50-300
		acifluorfen-sodium	50-300
	oxadiazoles		50-600
		oxadiargyl	50-600
	cyclic imides		0.5-300
		carfentrazone-ethyl	0.5-35
		cinidon-ethyl	3-35
		flumiclorac-pentyl	3-35
		butafenacil	5-300
		JV 485	50-300
C12 photosynthesis inhibitors			15-4000
	-	pyridate	250-1500
		pyridafol	250-1000
	benzothiadiazinones		30-1440
		bentazone	30-1440
	dipyridylenes		100–800
		paraquat–dichloride	100-800
	ureas		250-1600
		diuron	250-1600
		isoprotoron	250-1600
	phenols		100-700
		bromoxynil	100-700
	chloridazon		500-4000
	triazines		15-4000
		atrazine	15-4000

		terbutylazine	250-4000
	triazinone		30-300
		metribuzin	30-300
C13 synergists			500-1500
	oxiranes		500-1500
		tridiphane	500-1500
C14 growth substances			25-1200
	aryloxyalkanoic acids		50-1200
		fluoroxypyr	50-400
		MCPA	400-1200
		mecoprop-P	400-1200
	benzoic acids		75-800
		dicamba	75-800
	quinolinecarboxylic acids		25-600
		quinclorac	25-600
C16 various other herbicides	–	triaziflam	50–750

[a] If appropriate, 10-50 g/ha cloquintocet may also be added.

Use examples

The mixtures according to the invention were applied pre- or post-emergence (foliar treatment). The herbicidal compounds of component B and, if desired, of component C were applied in the formulation in which they are present as commercially available product.

The herbicidally active compounds of components A), B) and, if desired, C) were applied in succession or jointly, in the latter case in some cases as a tank mix and in some cases as a ready-mix, in the form of emulsions, aqueous solutions or suspensions, the vehicle being water (300 - 400 l/ha). In the case of the field trials, application was effected with the aid of a mobile plot sprayer.

The test period extended over 3 to 8 weeks, and the stands were also observed at later points in time.

Damage by the herbicidal compositions was evaluated with reference to a scale of 0% to 100% in comparison with untreated control plots. 0 means no damage and 100 means complete destruction of the plants.

The following examples will demonstrate the action of the herbicidal compositions which can be used according to the invention, without excluding the possibility of other uses.

In these examples, the value E at which only an additive effect of the individual active ingredients is to be expected was calculated by the method of S. R. Colby (Calculating synergistic and antagonistic responses of herbicide combinations, Weeds 15, 20 pp (1967)).

This was done using the formula

$$E = X + Y - \frac{XY}{100}$$

where

X = Percentage of the herbicidal action of X at an application rate of x;

Y = Percentage of the herbicidal action of Y at an application rate of Y;

E = expected herbicidal action of X + Y at rates of application x + y (in %);

or the formula

$$E = X + Y + Z - \frac{(XY + XZ + YZ)}{100} + \frac{XYZ}{10000}$$

where

X = Percentage of the herbicidal action of X at an application rate of x;

Y = Percentage of the herbicidal action of Y at an application rate of y;

Z = Percentage of the herbicidal action of Z at an application rate of Z;

E = expected herbicidal action of X + Y + Z at rates of application x + y + z (in %).

If the value observed exceeds the value E calculated in accordance with Colby's formula, then synergism is present.

The herbicidal mixtures according to the invention exert a greater herbicidal action than would have been expected according to Colby on the basis of the observed effects of the individual components when used alone.

The results of the tests are shown in Tables 3 to 17 below.

In these studies, the following plants were used:

Scientific name	Common name
Abutilon theophrasti	Velvetleaf
Amaranthus retroflexus	Pigweed
Avena fatua	Wild oat
Brachiaria plantaginea	Alexandergrass
Commelina benghalensis	Bengal commelina
Echinochloa crus-galli	Barnyardgrass
Galium aparine	Catchweed
Pharbitis purpurea	Common morningglory
Polygonum persicaria	Ladysthumb

Table 3: Herbicidal action of compound 1a.29 and imazapyr and imazethapyr[1] (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Abutilon theophrasti Damage [%]	Colby Value E
Ia.29	0.98	30	-
imazapyr + imazethapyr	0.98	20	-
Ia.29 + imazapyr + imazethapyr	0.98 + 0.98	55	44

Table 4: Herbicidal action of compound 1a.29 and imazapyr and imazethapyr[1] (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Commelina benghalensis Damage [%]	Colby Value E
Ia.29	3.91	50	-
imazapyr + imazethapyr	3.91	10	-
Ia.29 + imazapyr + imazethapyr	3.91 + 3.91	70	55

Table 5: Herbicidal action of compound 1a.29 and imazapic and imazapyr[2] (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Avena fatua Damage [%]	Colby Value E	Amaranthus retroflexus Damage [%]	Colby Value E
Ia.29	0.98	0	-	60	-
imazapic + imazapyr	0.98	10	-	20	-
Ia.29 + imazapic + imazapyr	0.98 + 0.98	40	10	75	68

Table 6: Herbicidal action of compound 1a.29 and imazapic and imazapyr[2] (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Avena fatua Damage [%]	Colby Value E
Ia.29	1.95	10	-
imazapic + imazapyr	1.95	25	-
Ia.29 + imazapic + imazapyr	1.95 + 1.95	60	33

Table 7: Herbicidal action of compound 1a.29, imazapyr and imazethapyr[1], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Amaranthus retroflexus Damage [%]	Colby Value E	Galium aparine Damage [%]	Colby Value E
Ia.29	0.98	60	-	20	-
imazapyr + imazethapyr	0.98	20	-	20	-
atrazine	15.6	40	-	0	-
Ia.29 + imazapyr + imazethapyr + atrazine	0.98 + 0.98 + 15.6	85	81	50	36

Table 8: Herbicidal action of compound 1a.29, imazapyr and imazethapyr[1], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Galium aparine Damage [%]	Colby Value E
Ia.29	1.95	30	-
imazapyr + imazethapyr	1.95	40	-
atrazine	31.25	20	-
Ia.29 + imazapyr + imazethapyr + atrazine	1.95 + 1.95 + 31.25	70	66

Table 9: Herbicidal action of compound 1a.29, imazapic and imazapyr[2], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Abutilon theophrasti Damage [%]	Colby Value E
Ia.29	7.81	85	-
imazapic + imazapyr	7.81	70	-
atrazine	125	30	-
Ia.29 +	7.81 +		

imazapic + imazapyr + atrazine	7.81 + 125	100	97

Table 10: Herbicidal action of compound 1a.29, imazapyr and imazethapyr[1], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Brachiaria plantaginea Damage [%]	Colby Value E	Echinochloa crus-galli Damage [%]	Colby Value E
Ia.29 + imazapyr + imazethapyr	7.81 + 7.81	85	-	80	-
Atrazine	125	25	-	30	
Ia.29 + imazapyr + imazethapyr + atrazine	7.81 + 7.81 + 125	100	89	100	86

Table 11: Herbicidal action of compound 1a.29, imazapyr and imazethapyr[1], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Galium aparine Damage [%]	Colby Value E	Polygonum persicaria Damage [%]	Colby Value E
Ia.29 + imazapyr + imazethapyr	7.81 + 7.81	70	-	75	-
atrazine	125	60	-	60	
Ia.29 + imazapyr + imazethapyr + atrazine	7.81 + 7.81 + 125	98	88	100	90

Table 12: Herbicidal action of compound 1a.29, imazapyr and imazethapyr[1], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Echinochloa crus-galli Damage [%]	Colby Value E	Pharbitis purpurea Damage [%]	Colby Value E
Ia.29 + imazapyr + imazethapyr	3.91 + 3.91	85	-	50	-
atrazine	62.5	20	-	80	

Ia.29 + imazapyr + imazethapyr + atrazine	3.91 + 3.91 + 62.5	95	88	100	90

Table 13: Herbicidal action of compound 1a.29, imazapyr and imazethapyr[1], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Polygonum persicaria Damage [%]	Colby Value E
Ia.29 + imazapyr + imazethapyr	3.91 + 3.91	70	-
atrazine	62.5	40	
Ia.29 + imazapyr + imazethapyr + atrazine	3.91 + 3.91 + 62.5	100	82

Table 14: Herbicidal action of compound Ia.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Echinochloa crus-galli Damage [%]	Colby Value E	Abutilon theophrasti Damage [%]	Colby Value E
Ia.29 + imazapic + imazapyr	7.81 + 7.81	80	-	85	-
atrazine	125	30	-	30	
Ia.29 + imazapic + imazapyr + atrazine	7.81 + 7.81 + 125	100	86	100	90

Table 15: Herbicidal action of compound Ia.29, imazapic and imazapyr², and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Galium aparine Damage [%]	Colby Value E
Ia.29 + imazapic + imazapyr	7.81 + 7.81	80	-
atrazine	125	60	

Ia.29 + imazapic + imazapyr + atrazine	7.81 + 7.81 + 125	98	92

Table 16: Herbicidal action of compound Ia.29, imazapic and imazapyr[2], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Brachiaria plantaginea Damage [%]	Colby Value E	Echinochloa crus-galli Damage [%]	Colby Value E
Ia.29 + imazapic + imazapyr	3.91 + 3.91	85	-	80	-
atrazine	62.5	20	-	20	
Ia.29 + imazapic + imazapyr + atrazine	3.91 + 3.91 + 62.5	100	88	98	84

Table 17: Herbicidal action of compound 1a.29, imazapic and imazapyr[2], and atrazine (post-emergence treatment; greenhouse)

	Application rate [g/ha ai]	Polygonum persicaria Damage [%]	Colby Value E
Ia.29 + imazapic + imazapyr	3.91 + 3.91	70	-
atrazine	62.5	40	
Ia.29 + imazapic + imazapyr + atrazine	3.91 + 3.91 + 62.5	100	82

[1] imazapyr : imazethapyr = 1 : 3

[2] imazapic : imazapyr = 3 : 1